

# Incommensurate Transverse Anisotropy Induced by Disorder and Spin-Orbit-Vibron Coupling in $Mn_{12}$ -acetate

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It has been shown within density-functional theory that in  $Mn_{12}$ -acetate there are effects due to disorder by solvent molecules and a coupling between vibrational and electronic degrees of freedom. We calculate the in-plane principal axes of the second-order anisotropy caused by the second effect and compare them with those of the fourth-order anisotropy due to the first effect. We find that the two types of the principal axes are not commensurate with each other, which results in a complete quenching of the tunnel-splitting oscillation as a function of an applied transverse field.

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The observation of resonant tunneling of magnetization in the single molecule magnet  $Mn_{12}$ -acetate<sup>1</sup> (hereafter  $Mn_{12}$ ) with a ground-state spin of  $S = 10$  has led to many experimental and theoretical investigations.<sup>2,3,4,5,6</sup> A simple anisotropy Hamiltonian for  $S = 10$  provides an excellent approximation to the physics occurring at low temperatures. Deriving the Hamiltonian from density-functional (DF) calculations is challenging but possible.<sup>4,5,6</sup> For a particular molecular geometry, a magnetic anisotropy tensor may be calculated considering spin-orbit coupling within a DF framework. In the principal-axes coordinates, the lowest-order spin Hamiltonian can be simplified to the following form:

$$\mathcal{H}_0 = DS_z^2 + E(S_x^2 - S_y^2), \quad (1)$$

where  $D$  and  $E$  are the uniaxial and second-order transverse anisotropy parameters and  $S_z$  is the easy-axis component of the spin operator  $S$ . The  $S_4$  symmetry of the ideal  $Mn_{12}$  molecule causes the value of  $E$  to vanish and the lowest-order transverse terms to be fourth order. Only transverse anisotropy terms are responsible for the resonant tunneling between energy levels that are almost degenerate. Magnetic tunneling measurements, however, showed that some of the resonant tunneling occurred at a level lower than fourth order.<sup>2</sup> To understand this anomaly in the tunneling, Cornia *et al.*<sup>7</sup> proposed that inherent disorder in solvent molecules may break the  $S_4$  symmetry and provide nonzero values of  $E$ . Recent electron paramagnetic resonance (EPR) experiments<sup>8,9</sup> and magnetic tunneling measurements<sup>9,10</sup> revealed that the model of Cornia *et al.*<sup>7</sup> needed to be refined for a quantitative comparison with experiment. Our DF calculations<sup>6</sup> on the  $Mn_{12}$  showed that the values of  $E$  for possible configurations of the disordered sol-

vent molecules are in good quantitative agreement with experiment.

For the  $Mn_{12}$ , the calculated  $D$  value is  $-0.556$  K,<sup>4</sup> which agrees well with experiment. The calculated (measured) value of  $D$ , however, does not account for all the measured anisotropy barrier of  $65$  K.<sup>3,8</sup> One needs a longitudinal anisotropy of order higher than second-order. In this spirit a fourth-order spin-orbit-vibron (SOV) interaction was proposed by Pederson *et al.*<sup>11</sup> Ideally, this SOV interaction can only contribute to modifying the second-order barrier and to activating two fourth-order transverse terms in the spin Hamiltonian. At this level a strong SOV interaction can complicate the tunneling experiments in several different ways. The simplest complication is that there are two different longitudinal 4th-order terms which scale as  $S^2 S_z^2$  and  $S_z^4$  respectively. If the  $S_z^4$  term is dominant, then at any resonant field only a single pair of states are involved with tunneling. The fourth-order transverse terms result in departures of the period of the tunnel-splitting oscillation from  $\Delta H_x = 2\sqrt{2E(|D| + E)}/g\mu_B$  that has been derived by Garg.<sup>12</sup> Such departures were first identified by Wernsdorfer *et al.*<sup>13</sup> and later modified to include the 4th-order transverse terms by the group of Garg.<sup>14</sup> Recent EPR and magnetic experiments<sup>9</sup> suggested that for  $Mn_{12}$  the in-plane principal axes of the second-order anisotropy may not be aligned with those of the fourth-order anisotropy so that the oscillation in the tunnel splitting could be completely quenched in this material, in contrast to Fe<sub>3</sub>[15].

In this paper, we perform the DF calculations on a statistically weighted collection of three different  $E$  values caused by the solvent disorder and on the fourth-order SOV interaction. We then combine these two effects to

determine whether DF theory (DFT) can qualitatively account for a suppression of oscillations in the tunnel splittings that occur in transverse tunneling experiments.

Our calculations have been performed within DFT using the NRLMOL program<sup>16</sup>. The NRLMOL calculates an accurate Gaussian-type orbital representation for the self-consistent occupied and unoccupied molecular orbitals. We use DFT within the generalized-gradient approximation<sup>17</sup> to account for the quantum-mechanical behavior of the electrons. The geometries of the molecules are fully relaxed. Considering the spin-orbit coupling for a relaxed geometry, as discussed in Ref. [4], the second-order anisotropy Hamiltonian ( $\sum_{a,b=x,y,z} \gamma_{ab} S_a S_b$ ) may be derived from the calculated orbitals. Diagonalization of the  $\gamma$  matrix provides the 2nd-order anisotropy barrier and the principal axes.

As shown in Fig. 1, a single  $\text{Mn}_{12}$  molecule is surrounded by four acetic-acid solvent molecules ( $\text{CH}_3\text{CO}_2\text{H}$ ), each of which is shared by two neighboring  $\text{Mn}_{12}$  molecules. If a  $\text{Mn}_{12}$  molecule is hydrogen-bonded to four  $\text{CH}_3\text{CO}_2\text{H}$  molecules as pictured in Fig. 1, then the symmetry of this molecule remains the same as  $S_4$ . Since  $\text{CH}_3\text{CO}_2\text{H}$  can bind to either of the  $\text{Mn}_{12}$  neighbors with the same energy, 1/16 of the  $\text{Mn}_{12}$  molecules have the  $S_4$ -symmetry with hydrogen bonds and another 1/16 of the molecules have the  $S_4$  symmetry *without* hydrogen bonds. The remaining molecules have different orientations which break the symmetry. As discussed in Ref. 6, there are a total of six different configurations which have the number of hydrogen bonds  $n$ , statistical weights, and  $D$  and  $E$  values of  $(0, 1/16, -0.54, 0.000)$ ,  $(4, 1/16, -0.56, 0.000)$ ,  $(1, 4/16, -0.54, 0.008)$ ,  $(2, 4/16, -0.55, 0.000)$ ,  $(2, 2/16, -0.55, 0.016)$ , and  $(3, 4/16, -0.55, 0.008)$ . The two distinctive cases of two hydrogen bondings are characterized by having neighboring acetic acids ("cis") hydrogen-bonded or next neighboring acetic acids ("trans") bonded, respectively. The  $S_4$  symmetry suggests that in the case of significantly small off-diagonal elements in the  $\gamma$  matrix for  $n = 1$ , the perturbations due to the "cis"-geometry should cancel each other and that those due to the "trans"-geometry should add constructively. Thus, we find that 5/8 of the molecules have appreciable  $E$  values of 0.008-0.016 K.

The Hamiltonian for a single uniaxial anisotropic spin coupled to a one-dimensional harmonic oscillator is given by  $\mathcal{H} = \gamma_{zz} S_z^2 + \frac{1}{2}(P^2 + \omega^2 Q^2) + Q \sum_{ab} \gamma'_{ab} S_a S_b$ , where  $P$ ,  $Q$ , and  $\omega$  are the momentum, position, and frequency of the oscillator and  $\gamma'_{ab} = d\gamma_{ab}/dQ$ . As shown in Ref. [11], the energy of the coupled system as a function of an eigenvalue of  $S_z$  ( $M$ ) is  $\mathcal{E} = \omega/2 + DM^2 - (A + BM^2)^2/2\omega^2$  where  $A = S(S+1)(\gamma'_{xx} + \gamma'_{yy})/2$  and  $B = \gamma'_{zz} - (\gamma'_{xx} + \gamma'_{yy})/2$ . Generalizing this problem to the  $\text{Mn}_{12}$  requires coupling all normal modes. In general, the fourth-order corrections to the Hamiltonian are  $\mathcal{H}_4 = \sum_{abcd} A_{abcd} S_a S_b S_c S_d$ . Only the Raman active vibrational modes lead to a change in the fourth-order barrier.

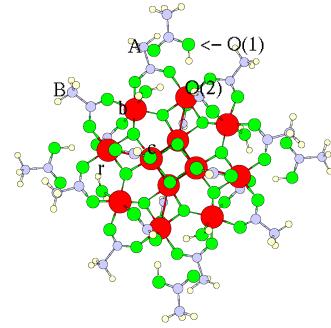


FIG. 1: Geometry of a  $\text{Mn}_{12}$  molecule with four hydrogen-bonded acetic acids molecules. This high-symmetry configuration accounts for only 1/16 of the total concentration. For details, see Ref.[6].

Combining the SOV interaction with the symmetry-breaking effects of the solvent disorder, we can write the total spin Hamiltonian as:

$$\mathcal{H} = DS_z^2 + E[\cos(2\alpha)(S_x^2 - S_y^2) + 2\sin(2\alpha)S_x S_y] + A_1 S_z^2 (S_z^2 - S_z^2/3) + A_2 [3S^4 + 35S_z^4 - 30S_z^2 S_z^2] + B_1 (S_x^4 + S_y^4 - 6S_x^2 S_y^2) + B_2 [S_x S_y (S_x^2 - S_y^2)] \quad (2)$$

where  $\alpha$  denotes the angle between the medium axes of the calculated second-order and fourth-order anisotropy and  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$  represent fourth-order anisotropy parameters. If one replaces the operators  $(S_x, S_y, S_z)$  by classical spin vectors and recast the fourth-order transverse terms in spherical coordinates, then the classical potential energy in the  $xy$  plane (e.g.  $\theta = \pi/2$ ) becomes

$$\mathcal{E} = \mathcal{E}_0 + S^4 [B_1 \cos(4\phi) + \frac{B_2}{4} \sin(4\phi)], \quad (3)$$

where  $\mathcal{E}_0$  is a constant term and  $\phi$  is the azimuthal angle. This shows that the energy surface of a system with  $S_4$  symmetry, at fourth order, resembles a four-leaf clover in the  $xy$  plane. Furthermore, when the fourth-order terms in Eq. (3) are accounted for, the in-plane principal axes are determined to lie along the nodes or antinodes of the classical potential. In addition, once  $B_1$  and  $B_2$  are determined in given coordinates, a rotation by  $\cos^{-1}[B_1/(B_1^2 + B_2^2/16)^{1/2}]$  allows one to re-express the two transverse terms as  $C(S_+^4 + S_-^4)$  with  $C = [B_1^2 + B_2^2/16]^{1/2}/2$ . The experimental value of  $C$  is  $2.3 \times 10^{-5}$  K,<sup>8</sup> while the SOV contributions to  $B_1$  and  $B_2$  lead to  $C_{\text{sov}} = 0.053 \times 10^{-5}$  K.<sup>11</sup>

Even with the rotation of the  $B_1$  and  $B_2$  terms to the more usual definition, the 2nd-order transverse terms may not, in general, be simultaneously expressed in the diagonal form. So the dependence on  $\alpha$  is required. To compute  $\alpha$  we calculate the separate magnetic anisotropy energies from the SOV interaction and the solvent disorder as a function of  $\phi$  in the  $xy$  plane. For the solvent disorder only three configurations [ $n = 1, 2$  (trans), and 3] are considered in the calculation because the rest of

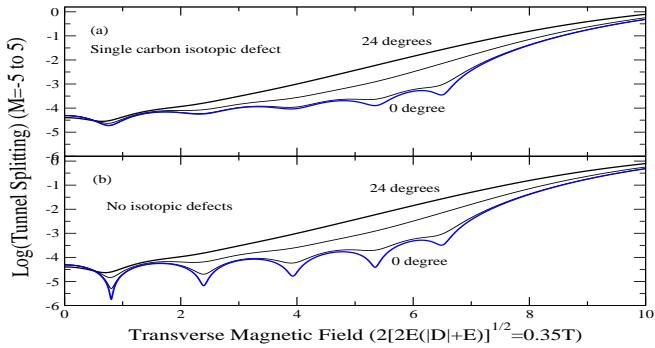


FIG. 2: Logarithm of the  $M = \pm 5$  tunnel splitting versus applied transverse field for a  $\text{Mn}_{12}$  with one  $^{13}\text{C}$  isotopic defect and pure  $\text{Mn}_{12}$ . Different values for  $\alpha$  (0, 3, 12, and  $24^\circ$ ) were used.

the three configurations do not produce  $E$ . We find that  $\alpha$  is  $24^\circ$ . This is a bit smaller than the experimentally measured value of  $\alpha = 27^\circ$ .<sup>9</sup> We calculate the tunnel splitting between  $M = -5$  and  $M = 5$  with various values of  $\alpha$  in zero field from diagonalizing the quantum mechanical form of Eq. (2) which takes into account the non-commutativity of the spin operators. For the pure  $\text{Mn}_{12}$  sample we find that the oscillation in the tunnel splitting is entirely quenched at the calculated value of  $\alpha = 24^\circ$  as shown in Fig. 2(b). When  $\alpha = 0$ , as expected from  $\text{Fe}_8$ ,<sup>15</sup> the oscillation is clearly visible. Even for a very small value of  $\alpha$  such as  $3^\circ$ , the amplitude of the oscillation tends to be mostly damped out. As the applied transverse field increases, the effect of the incommensurate transverse anisotropy decreases because the tunneling is governed by a strong transverse field. Because of the fourth-order terms in Eq. (2), the period of the oscillation decreases as the transverse field increases.<sup>14</sup>

For a naturally occurring collection of  $\text{Mn}_{12}$  molecules,

37% of the molecules contain one or two isotopic defects. In the case of isotopic defects in the  $\text{Mn}_{12}$ , the SOV interaction provides additional symmetry-breaking in the spin Hamiltonian. If the SOV interaction is large enough, this fraction of molecules would contribute to an almost continuous distribution of broken-symmetry anisotropy Hamiltonians. We calculate the same tunnel splitting for the  $\text{Mn}_{12}$  doped with one carbon isotope ( $^{13}\text{C}$ ) for various values of  $\alpha$  [Fig. 2(a)]. We find that even one isotopic defect substantially suppresses the oscillation in the tunnel splitting but the period remains unperturbed. Since the tunneling experiments were performed in the presence of the longitudinal field that makes  $M$  and  $M'$  almost degenerate where  $M + M' \neq 0$ , direct comparison with experiment is not possible. The effect of the longitudinal field and the different types of isotopic defects on the tunnel-splitting is in progress.

In summary, for  $\text{Mn}_{12}$  we have considered the second-order anisotropy induced by the disordered solvent molecules and the fourth-order SOV interaction within the DFT framework. The second-order transverse terms could cause the oscillation in the tunnel splitting. Experimental data indicated that the in-plane principal axes of the second-order anisotropy was not commensurate with those of the fourth-order anisotropy. DFT calculations showed that the angle between the two types of anisotropy and resulting quenching of the oscillation agree well with experiment.

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